Partial Electron Transfer in Octadecanethiol Binding to Gold†

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Langmuir-Blodgett transfer of octadecanethiol (C18SH) containing monolayers onto gold-coated glass slides under potentiostatic conditions leads to a quantitative characterization of C18SH chemisorption on gold. The thiol-gold bond involves a partial electron transfer from sulfur to the gold substrate. The C18SH partial charge number was determined to vary linearly with the potential of gold substrates from 0.30 at −0.30 V to 0.45 at 0.70 V vs SCE. Only ca. 81% of C18SH molecules appear to chemisorb upon LB transfer at 20 mN/m. This is likely a result of some orientational restrictions (e.g., tilt and registry with the gold surface lattice) imposed on the system by the lateral pressure during LB transfer. The requirement of monolayer charge neutrality, stemming from a negligible capacitance of the Au/LB monolayer interface, results in a dissociation of thiol’s proton to an extent equal to the charge transferred due to C18SH chemisorption.

Introduction

The well-ordered structure, simplicity of preparation, and wide ranging applications of self-assembled alkanethiol monolayers on gold surfaces have attracted considerable interest of scientists from a spectrum of fields, from chemical physicists1−4 to organic6−12 and analytical13−24 chemists. This relatively new area is already a subject of several reviews,25−28 Research in this area has been concerned, to a large extent, with structural characterization of the monolayers of n-alkanethiols, disulfides, and their derivatives on gold, silver, and other metal surfaces.1−5,27,29−35 Related research involves earlier studies of self-assembled alkytrichlorosilane monolayers36,37 and Langmuir-Blodgett films.38,39 These monolayer structures have been used to model and to investigate interfacial properties of biological membranes and organic materials in processes and phenomena such as molecular recognition, ion-transport, wettability, adhesion, friction, biocompatibility, and others. Structural stability and molecular order of alkanethiol monolayers on gold allowed systematic studies of long range electron transfer30,39−41 and opened a number of possibilities in designing chemical sensors.21−24,44,45

Formation of the sulfur−gold bond in alkanethiol self-assembly is, naturally, the process of fundamental importance to a large fraction of research mentioned above. Surprisingly, then, the understanding of some key mechanistic elements involved in this reaction still remains incomplete and controversial.15,28,46−53 Specifically, XPS

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data supported by IR spectroscopy were used to suggest that chemisorption of alkanethiols on gold(0) surface results in the formation of gold(I) thiolate denoted as either \( \text{RS}^\text{-Au}(I) \) or \( \text{RS}^\text{+Au} \). It has then been postulated that this general mechanism requires loss of hydrogen as \( \text{H}_2 \) (eq 1), formation of water (eq 2), or of some other products of the surface oxidation such as hydrogen peroxide (eq 3).

\[
\begin{align*}
\text{RS} + \text{Au}(0) & \rightarrow \text{RS}^\text{-Au}(I) + \frac{1}{2}\text{H}_2 \\
2\text{RS} + 2\text{Au}(0) & + \frac{1}{2}\text{O}_2 \rightarrow 2\text{RS}^\text{-Au}(I) + \text{H}_2\text{O} \\
2\text{RS} + 2\text{Au}(0) & + \text{O}_2 \rightarrow 2\text{RS}^\text{+Au} + \text{H}_2\text{O}_2
\end{align*}
\]

Indeed, \( \text{H}_2\text{O}_2 \) was detected in one study involving self-assembly of propanethiol on gold powder in an oxygen-saturated aqueous solution. Its release was postulated to be a result of \( \text{O}_2 \) and \( \text{H}_2 \) reaction following reaction 1. The mechanistic schemes presented above seem to be supported by the measurements of surface potential and by the electrochemical studies of alkanethiol reductive desorption. Recent laser desorption mass spectrometric studies point at the chemisorption of alkanethiols rather than alkanethiolates. Temperature-programmed desorption spectra of monolayers of alkanethiol and dimethyl sulfoxide on gold(111) allowed estimation of the binding energy of the former to be 12-14 kcal/mol (indicating physisorption) while the \( \text{S}-\text{Au} \) bond strength (charge per thiol molecule) is a linear function of the character of this bond and the identity, or even presence, of the products of the surface oxidation reaction (eqs 1-3) are not well known.

In this report, we present a novel electrochemical method which combines Langmuir—Blodgett transfer technique with either potential (at open circuit) or current measurements (under potentiostatic conditions). This method allows us to determine that the primary step of alkanethiol chemisorption involves a partial electron transfer from thiol to gold. The partial charge number (charge per thiol molecule) is a linear function of the potential of gold substrate and varies from 0.30 electron within 1 week from their fabrication. Immediately before the experiments and imprinted with the use of thin aluminum masks. Subsequently, they were boiled in 50:30:20 2-propanoVmethanol-chloroform mixture, dried again, and transferred to the evaporation vessel. The reaction of any scratches or blemishes. The cleaning procedure involved rinsing with organic solvents (methanol, acetone, 2-propanol, chloroform) and Nanopure water. Subsequently, gold electrodes were specially designed for the LB electrochemical experiments and imprinted with the use of thin aluminum masks. The pattern is shown in Figure 1 (for a full description see text in Results and Discussion). The surface area of its central rectangular fragment was 0.20 cm². Prior to the vacuum deposition of Cr and Au films, glass slides were washed in chromic acid, rinsed thoroughly in Nanopure water, and then dried. Subsequently, they were boiled in 50:30:20 2-propanol/methanol/chloroform mixture, dried again, and transferred to the evaporator (Veeco 7700). After fabrication, vapor-deposited electrodes were transferred and stored in a vacuum desicator. They were used in the Langmuir—Blodgett (LB) experiments typically within 1 week from their fabrication. Immediately before the LB experiments, gold electrodes were visually examined to select those free of any scratches or blemishes. The cleaning procedure involved rinsing with organic solvents (methanol, acetone, 2-propanol, chloroform) and Nanopure water. Subsequently, gold electrodes were immersed into a fresh, hot (ca. 80 °C) chromic acid solution for about 5-10 A/s. A 6-10 nm thick chromium underlayer was evaporated first to provide good adhesion and stability of the gold layer. The geometrical pattern of the vapor-deposited electrodes was specially designed for the LB electrochemical experiments and imprinted with the use of thin aluminum masks.

Electrode Fabrication Procedures. Electrodes were produced by vapor deposition of about 100 nm thick gold films (99.95% Au, Lawrence Berkeley Laboratory) on microscope glass slides (Corning Plain Micro Slides). The rate of deposition was ca. 5-10 A/s. A 6-10 nm thick chromium underlayer was evaporated first to provide good adhesion and stability of the gold layer. The geometrical pattern of the vapor-deposited electrodes was specially designed for the LB electrochemical experiments and imprinted with the use of thin aluminum masks. The pattern is shown in Figure 1 (for a full description see text in Results and Discussion). The surface area of its central rectangular fragment was 0.20 cm². Prior to the vacuum deposition of Cr and Au films, glass slides were washed in chromic acid, rinsed thoroughly in Nanopure water, and then dried. Subsequently, they were boiled in 50:30:20 2-propanol/methanol/chloroform mixture, dried again, and transferred to the evaporator (Veeco 7700). After fabrication, vapor-deposited electrodes were transferred and stored in a vacuum desicator. They were used in the Langmuir—Blodgett (LB) experiments typically within 1 week from their fabrication. Immediately before the LB experiments, gold electrodes were visually examined to select those free of any scratches or blemishes. The cleaning procedure involved rinsing with organic solvents (methanol, acetone, 2-propanol, chloroform) and Nanopure water. Subsequently, gold electrodes were immersed into a fresh, hot (ca. 80 °C) chromic acid solution for about 25 s. The chromic acid treatment step was followed by an extensive rinsing with Nanopure water. Upon completion of this step, the electrodes were dried in a stream of argon and transferred immediately (in order to minimize their contamination) into the Plexiglas enclosure of the LB instrument. Before each LB transfer experiment, the surface of a gold substrate was electrochemically reduced and conditioned by voltammetric scanning in the potential range from \(-0.300 \) to \(0.600 \) V at \(50 \text{ mV/s} \) directly in the subphase in the LB trough. In the case of potentiometric experiments, the voltammetric cycling was stopped at \(0.0 \) V during an anodic scan, and then the
potentiostat was switched to open circuit conditions. The gold substrates were allowed typically 10 min to attain a stable potential value. Similarly, in the case of the potentiostatic experiments, each potential value selected for a particular LB transfer experiment was applied by interrupting an anodic scan.

**Langmuir—Blodgett Procedures.** The Langmuir—Blodgett experiments were carried out with a KSV Minitrough instrument operated under computer control. Routine Langmuir—Blodgett procedures and the LB transfer protocol were described previously. C16SH/C18OH monolayers were spread as chloroform solutions at a surface concentration corresponding to 95 Å²/molecule. Following solvent evaporation, the monolayers were compressed at a rate of ca. 4 Å²/(molecule/min) to a pressure of 20 mN/m. The LB transfers were carried out at that pressure at a rate of 10 mm/min unless specified otherwise.

**Instrumentation.** The potential control of the gold electrode substrates and current measurements during LB transfer experiments were accomplished with a three-electrode potentiostat (CV 27 by BAS, Inc., West Lafayette, IN). The potentiometric measurements were done with the same instrument operated at open circuit. The counter and reference (SCE) electrodes were placed in the LB trough behind the moving barrier to prevent their interference with the monolayer compression and transfer. In order to avoid Cl⁻ leakage, the reference electrode was isolated from the subphase in the LB trough via a salt bridge filled with the same electrolyte at that in the trough. The current/potential, current/time and potential/time data were recorded on a X-Y recorder.

**Results and Discussion**

**Langmuir—Blodgett Transfer under Potentiometric Conditions.** The experiments described in this and the following sections concern standard LB transfers of octadecane alcohol (C16OH) and mixed octadecane alcohol and octadecanethiol (C16SH) monolayers from the water surface onto gold substrates fabricated by vapor deposition of 100 nm thick gold films on glass slides (see Experimental Section). Behavior of Langmuir monolayers of C16OH on the water surface is well-known in the literature. Pure C16SH cannot be compressed on the aqueous subphase above ca. 12 mN/m due to insufficient polarity of the thiol group. We showed earlier that C16SH and C16OH are fully miscible in their mixed monolayers which combine the properties of the individual components. Specifically, the collapse pressure of the mixed system increases linearly with the increased mole fraction of C16OH. All LB transfer experiments discussed below were carried out at 20 mN/m. To accomplish this, the C16SH mole fraction must not exceed 70%. Figure 1 shows schematically an LB experiment with potentiometric monitoring of the gold substrate. In an LB experiment, a solid substrate is slowly pulled vertically up from the aqueous subphase across the water/air interface. This results in a transfer of a monolayer from the water surface onto the substrate’s surface. During the LB transfer, the monolayer on the water surface is maintained at a selected constant surface pressure by the forward motion of the barrier of the Langmuir trough controlled by the feedback mechanism of the instrument. As we show below, the transfer of both C16OH and C16SH/C18OH monolayers can be classified as, so-called, reactive transfer where the surfactant molecules interact directly with the substrate’s surface at the moment of transfer. The nonreactive transfer involves a transfer of a monolayer onto a thin film of water which subsequently is squeezed out as the monolayer is deposited on the surface of the substrate. In the latter case, the dynamic contact angle observed during the LB transfer, θ, is essentially zero while its value is significantly greater than zero during a reactive transfer leading to a lower water meniscus. The values of θ observed on the gold surface in our experiment were approximately 70° and 80° for C16OH and C16SH/C18OH monolayers, respectively. Since the dynamic contact angles on the glass surface are close to zero, it is difficult to make a precise assessment of θ on gold. Nevertheless, the high values reported above clearly demonstrate the reactive character of the monolayer transfer of gold.

The geometric pattern of the vapor-deposited gold films on glass slides used in our experiments is shown in Figure 1. The lines coinciding with the top and the bottom edge of the central rectangular part of the electrode mark the initial and the final positions of the water meniscus in all experiments. Thus, the top circular area was always kept above the water surface and used to make the electrical contact while the bottom circular area was always submerged in the aqueous subphase. In the course of each LB experiment, the rectangular part was withdrawn above the water surface at a constant rate (typically 10 mm/min) while coating it with a monolayer from the water surface. Figure 2 shows two typical recordings of the potential of the gold substrate monitored during the LB transfer experiments carried out on 0.05 M HClO₄ subphase. In both cases of C16OH and C16SH/C18OH (70:30 mol %) monolayers, the initial open circuit potential of the gold substrates was ca. 0.13 V vs SCE. Gold substrates approximately reach this value in the course of a 10 min equilibration in the subphase. As we show in the next section, this value of a stable open circuit potential is approximately 0.21 V negative of the potential of zero charge (PZC) of the gold substrate.

Consider first the potential-time trace obtained during LB transfer of C16OH monolayer. Independent measurements showed that the transfer ratio of C16OH under these conditions is 1.0 ± 0.05. A linear decrease of the electrode potential is observed (Figure 2) during the withdrawal of

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the rectangular section, followed by a gradual increase of the electrode potential after the completion of the LB transfer when the entire rectangular area of the electrode was brought above the water surface. Since the initial potential of the gold substrate is negative of PZC, the observed decrease of the potential is consistent with an increase of the negative excess charge density on the gold surface remaining under water caused by a shift of the excess negative charge from the upper part of the electrode. In other words, as the C,H monolayer is deposited on the rectangular section of the gold substrate and the latter is emersed dry from the electrolyte solution, the excess negative charge stored at that interface is “squeezed” down to the interface remaining under water and leads to the observed decrease of the potential.

The double-layer charge “squeezing” observed in this experiment merely reflects the large difference between the interfacial capacitance of the clean gold electrode immersed in 0.05 M HClO₄ (ca. 20 pF/cm²) and that of the gold surface coated with C₈H monolayer in the air. The latter can be assumed to be negligibly small. This assumption is well justified since the interfacial capacitance of the gold surface coated with octadecanethiol or similar monolayer assemblies in aqueous electrolyte is only ca. 1.0 μF/cm². Thus the situation at the end of the experiment, when only the lower part of the electrode remains under water and stores all the charge, can be represented in terms of an equivalent circuit in Scheme 1 with C₁ ≪ C₂ (since C₁ ∼ 0), where C₁ and C₂ represent interfacial capacitances of the Au/C₈H/air and Au/0.05 M HClO₄ interfaces, respectively. Naturally, the amount of charge accumulated in each of the two capacitors will be directly proportional to the magnitude of their capacitances. Hence, essentially no charge can be stored at the Au/C₈H/air interface. Implications of this important point will be seen in the sections below.

The gradual increase of the electrode potential observed after the LB transfer when the electrode is held in its upper-most position (see insert in Figure 1) is due, most probably, to a background faradaic process that slowly consumes the negative excess charge. The very high input impedance of the potentiometer (> 10⁶ Ω) eliminates the possibility of instrument “leakage” current as a reason for the observed potential increase.

Let us consider now the second potential—time trace in Figure 2 corresponding to the LB transfer of a mixed C₁₈SH/C₈H monolayer. Unlike aliphatic alcohols, for which weak physisorption on gold does not involve partial electron transfer, chemisorption of alkanethiols is naturally expected to result in much stronger interactions. Hence, in this case, we postulate that a much larger decrease of the gold substrate potential is due to two factors: (1) the double-layer charge “squeezing” as above and (2) electron transfer from C₁₈SH molecules to gold substrate as they bind to its surface. Thus, we postulate that the primary event in the C₁₈SH—gold bond formation can be represented by the reaction

\[
\text{C}_1 \equiv 0
\]

\[
\text{C}_2 \gg \text{C}_1
\]

(4)

where \( \delta \) is the partial charge number expressing the order and the strength of this bond per alkanethiol molecule. Additional mechanistic steps accompanying the partial electron transfer are discussed below. In view of the notation used in eqs 1–3, it is perhaps worth pointing out that no distinction is made between gold atoms on the surface, as far as electron energetics are concerned, whether they engage or do not engage in thiol—gold bond formation. Electron energy at the gold surface is expressed by the electrode potential.

As explained above, charge stemming from both double-layer charge “squeezing” and C₁₈SH binding accumulates at the clean gold/electrolyte interface resulting in a more significant negative shift of the potential as shown in Figure 2.

**Langmuir—Blodgett Transfer under Constant Potential Conditions: C₁₈H Monolayers.** Quantitative interpretation of the changes of the potential of the gold substrate in order to obtain the partial charge number of C₁₈SH on gold requires the exact value of the double-layer capacitance of the gold/electrolyte surface and its dependence on the electrode potential. It is therefore more convenient to carry out the experiments of Figure 2 under constant potential conditions. In those experiments, a three-electrode potentiostat was used. The gold substrate was connected as a working electrode. As previously, LB transfer of the C₁₈H monolayer results in “squeezing” of the double-layer charge upon emersion of a dry gold substrate. In this case, however, excess charge removed from the emersed gold surface cannot accumulate at the part of the electrode under water since its potential is kept constant by the potentiostat. Instead, the double-layer charge is collected and recorded as discharging current, \( i_{dis} \). A typical current—time trace recorded at 0.10 V vs SCE in the course of LB transfer of C₁₈H OH is shown in Figure 3. The observed current can be simply expressed by

\[
i_{dis} = \omega M \frac{dA}{dt}
\]

where \( \omega M \) is the excess charge density on the gold surface immersed in the electrolyte solution (before the LB transfer) and \( \frac{dA}{dt} \) is the rate of surface erosion (in cm²/s) during the LB transfer. Since the latter is an adjustable parameter, the observed current gives the double-layer charge density. (In practice, \( \omega M \) was obtained by integration of the current transient above background.) As expected, \( i_{dis} \) is linearly proportional to the rate of withdrawal of the electrode surface, \( \frac{dA}{dt} \) (see Figure 4), as long as the LB transfer rate is less than 50 mm/min.

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50. The magnitude of the potential decrease observed in such experiment is independent of the presence or absence of oxygen in the subphase electrolyte.

A negative deviation observed at 50 mm/min marks a breakdown of this experiment, as some electrolyte is entrapped on the gold surface during LB transfer. This results in an incomplete removal of the double-layer charge.

The plot of the double-layer charge density vs potential obtained in these experiments is shown in Figure 5 (closed squares). It is possible to approximate these data by a straight line. The crossing point of the linear regression line with the potential axis gives an estimate of PZC of 0.20 V vs SCE. The bar indicates the average standard deviation, for all the measurements, of 1.25 μC/cm².

Figure 3. Typical current–time transients recorded during LB transfer of C₁₈OH and C₁₈SH/C₁₈OH (70:30 mol %) monolayers at 20 mN/m, from 0.05 M HClO₄ subphase onto gold-coated glass slides held at 0.20 V vs SCE. LB transfer rate was 10 mm/min (corresponding to dQ/dt = 0.4 cm²/min).

Figure 4. Plot of current vs transfer rate recorded during LB transfer of C₁₈OH monolayers from 0.05 M HClO₄ onto 0.2 cm² gold-coated glass substrates at 0.20 V vs SCE.

The slope of the surface excess charge density vs potential plot in Figure 5 provides the integral capacitance value of ca. 14 μF/cm². This value appears to be low compared to ca. 20 μF/cm² that could be obtained over the same potential range from the literature data for single crystal gold(111) surfaces. Knowing that double-layer capacitance is very sensitive to the structure of the electrode surface, traces of impurities, and the type and concentration of the electrolyte, we believe that this discrepancy is not unusual, considering all the differences in the experimental conditions between our system and the reference systems in the literature. Overall, then, our charge density data in Figure 5 are reasonably consistent with the literature values. This, together with the proportionality of iₑₑ with the LB transfer rate (Figure 4), assures us that the LB transfer of C₁₈OH results in an approximately complete removal of the double-layer charge as gold substrates are emersed dry from the electrolyte solution.
LB Transfer of Mixed C_{18}SH/C_{18}OH Monolayer under Controlled Potential Conditions. Consider now the results of the potentiostatic LB transfer experiments obtained with mixed C_{18}SH/C_{18}OH monolayers (see Figures 3 and 5). As expected on the basis of the discussion in the previous section, when these experiments are carried out at $E < \text{PZC}$, a substantially higher current is observed. At constant potential, current due to C_{18}SH binding to gold is added to the double-layer discharging current. Naturally, at the potentials positive of PZC, the two current components are of the opposite sign. Using the same procedure of data analysis as above, we obtained the total charge collected during the LB transfer experiments (see Figure 5 open circles). By subtracting from the latter series the values of the double layer charge density, we obtained the dependence of the charge transferred due to C_{18}SH binding to gold vs the potential of the gold substrate (Figure 5, closed circles).

In order to obtain the apparent partial charge number ($\delta$), i.e. the fraction of electron charge transferred by each C_{18}SH molecule (assuming their 100% activity—see discussion below), we measured the geometric transfer ratio (the ratio of the surface area of the monolayer removed from the water surface to the geometric surface area of the gold substrate coated with the monolayer). Large (3 in. × 1 in.) glass slides coated with gold on both sides were used in these experiments. A transfer ratio of 0.98 ± 0.06 was obtained by averaging data obtained with four different substrates. Knowing the transfer ratio and the mean molecular area of the molecules on the water surface at the LB transfer pressure (20.1 ± 0.3 Å²/molecule), we obtained the apparent C_{18}SH partial charge number (see Figure 5, closed circles and the right-hand side ordinate). The latter exhibits a weak, roughly linear dependence on the potential of gold substrates increasing from 0.25 at −0.3 V to 0.36 at 0.7 V vs SCE.

The data at potentials greater than 0.7 V are strongly affected by the formation of gold oxide species and by the direct electro-oxidation of C_{18}SH. Thiol derivatives are known to be electro-oxidized from an adsorbed state on gold electrodes in this range of potentials.\(^{69,70}\) Oxidative desorption of propanethiol from gold yielding propanesulfonic acid was observed recently by Widrig and co-workers.\(^{30}\) Some additional experiments carried out in this potential range will be presented in a separate report.

We consider now some mechanistic implications that can be derived from the data presented above. The net charge recorded in the potential range from −0.3 to 0.7 V (closed circles in Figure 5) reflects the partial electron transfer from thiol to gold as stated in eq 4 above. Thus we can say that under our experimental conditions C_{18}SH chemisorption results in the formation of a weak coordination bond with the surface gold atoms, involving a transfer of approximately 0.24 to 0.36 electron (depending on the potential of the gold substrate, and assuming that all C_{18}SH transferred chemisorb) per alkanethiol molecule. It becomes important to realize that this would leave approximately +0.3 charge on each thiol group as the C_{18}SH monolayer is transferred onto the gold surface. In view of the fact that the capacitance of the interface above water is essentially zero (see Scheme 1 and the related discussion above), a charge of this magnitude clearly cannot exist at the interface under these conditions. Explicitly, the condition of negligible capacitance of the interface means that no charge can be stored on either the metal or the monolayer side of the interface. Since no counterions can be transferred with the C_{18}SH/C_{18}OH monolayer to match this charge (perchlorate ions are the only anions in the subphase and their transfer as counterions is sterically impossible and inconsistent with the transfer ratio reported above), we postulate that an equivalent quantity of protons is released from the monolayer as C_{18}SH molecules are transferred and bound to the gold substrate. This is the only way that the system can maintain charge neutrality of the C_{18}SH monolayer above the water surface. We note that the postulated proton dissociation is consistent with the expected weakening of the $-S-H$ bond upon thiol binding to gold. It is also consistent with several Raman,\(^{81,71}\) IR,\(^{82}\) and mass\(^{54}\) spectroscopic studies of self-assembled alkanethiol monolayer on gold showing absence of the thiol proton.

In a related Raman investigation, absence of the thiol proton was also reported in chemisorption of 6-mercapto-1-purine on gold electrodes.\(^{72}\) We should stress again that in our experiments the proton dissociation takes place primarily to maintain the required charge neutrality of the monolayer, and, thus, is a consequence of, rather than a prerequisite to, the thiol–gold bond formation. Its extent is linked directly to the magnitude of the partial charge number. The extent of proton dissociation during alkanethiol self-assembly experiments may be different or, indeed, complete due to the differences in the prevailing conditions of the interfacial capacitance, presence of traces of ionic species, etc. Recent \textit{ab initio} geometry optimization of CH₃S on Au(111) and Au(100) surfaces by Ulman and co-workers modeling alkanethiol chemisorption predicts −0.7 electron charge on sulfur atom bound to top sites and −0.4 charge for those bound to 3-fold hollow sites on gold(111).\(^{73}\)

\textbf{Extent of C_{18}SH Chemisorption upon LB Transfer of C_{18}SH/C_{18}OH Monolayers on Gold.} Considering the mechanics of the potentiostatic LB experiments, it is only fair to ask whether all C_{18}SH molecules transferred from the water surface bind to the gold surface on the time scale allowed by the LB transfer rate (≤30 s). In other words: how well do we approximate the equilibrium conditions of self-assembly? To answer these questions, it is interesting to point out that LB transfer (under "reactive" conditions) can be considered as a 2-D equivalent of self-assembly. In the LB transfer, a one-dimensional "section" of a surface or a "line" of gold is exposed to a two-dimensional condensed system of the assembling molecules. That exposure time is admittedly only ca. 6 μs (for a 10 Å wide "line" with the transfer rate of 10 mm/min used in these experiments). However, there are two important characteristics of LB transfer that weight heavily toward acceleration of the "2-D self-assembly". The first one is the concentration of C_{18}SH in a monolayer at 20 mN/m which is effectively several orders of magnitude larger than those used typically in solution self-assembly experiments. The second, even more important factor, is the fact that in the LB process, the surface is exposed to an already well-ordered array of C_{18}SH molecules. In the conventional self-assembly experiments carried out in 1 mM ethanol solutions of octadecanethiol, Bain and co-workers observed close to the limiting contact angles on gold surfaces in less than 1 min and proposed that the self-assembly process proceeds in two distinct phases.\(^{14}\) This was recently confirmed by near-edge XAFS.

\(^{(69)}\) Korytka, J.; Pradac, J. J. Electroanal. Chem. 1988, 17, 177.
ments bind to its surface. Self-assembly of octadecanethiol (C18SH) molecules transferred bind to gold. The latter issue directly addresses the question whether all C18SH molecules transferred bind to gold. In the third set of experiments, we have examined the reactive nature of the LB transfer of the C18SH/Cl18H monolayers. However, comparison of the transfer ratios and the QLB values for the two most roughened substrates (entries 4 and 5) indicates that monolayer transfer on excessively rough surfaces no longer follows the microscopic contour of the surface.

The variation of the apparent partial charge number (δ) with surface roughness is the key feature of the data in Table 1. It is clear that δ is higher on rough surfaces relative to Au/glass. As expected, the LB transfer ratios and the charge due to C18SH chemisorption (Q0°) increase with the substrate roughness. This is consistent with the reactive nature of the LB transfer of the C18SH/Cl18H monolayers. However, comparison of the transfer ratios and the QLB values for the two most roughened substrates (entries 4 and 5) indicates that monolayer transfer on excessively rough surfaces no longer follows the microscopic contour of the surface.

Table 1. Dependence of the C18SH Partial Charge Number and the C18SH/Cl18H LB Transfer Ratio on the Roughness of Gold Substrates

<table>
<thead>
<tr>
<th>Substrate Type</th>
<th>C18SH Partial Charge Number (Q0°)</th>
<th>C18SH LB Transfer Ratio (QLB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/glass</td>
<td>1.00</td>
<td>352</td>
</tr>
<tr>
<td>Au foil</td>
<td>1.09</td>
<td>385</td>
</tr>
<tr>
<td>Au foil</td>
<td>1.22</td>
<td>428</td>
</tr>
<tr>
<td>Au foil roughened</td>
<td>1.35 ± 0.08</td>
<td>619</td>
</tr>
<tr>
<td>Au foil roughened</td>
<td>1.35 ± 0.08</td>
<td>1150</td>
</tr>
</tbody>
</table>

*Charge due to the electroreduction of the surface gold oxide film produced in an anodic voltammetric scan extended to +1.3 V vs SCE in 0.05 M HClO4. Charge due to C18SH chemisorption obtained during potentiostatic LB experiments at +0.30 V vs SCE.

The gold oxide charge (Q0°) in the second column illustrates an increase of true surface roughness of the gold substrates. The original surface was smooth but not optically flat. To further increase the extent of surface roughness, we followed a procedure involving repetitive voltammetric cycling of the gold substrates between +1.2 V and −0.3 V vs SCE in 0.1 M KCl. The variation of the apparent partial charge number (δ) with surface roughness is the key feature of the data in Table 1. It is clear that δ is higher on rough surfaces compared to relatively smooth Au/glass substrates for which roughness factor is known to be ca. 1.2.50 In view of the finite precision of these measurements, we believe that there are no significant differences between the δ values for the entries 3, 4, and 5 in Table 1. Therefore, we will use their average of 0.36 ± 0.03. Since this average

Figure 6. Plots of current and the corresponding charge density vs transfer rate recorded during LB transfer of C18SH/Cl18H (70:30 mol %) monolayers from 0.05 M HClO4 at 0.0 V vs SCE.

Figure 7. Plot of the total charge collected during LB transfer (10 mm/min) of C18SH/Cl18H monolayers from 0.05 M HClO4 on gold substrates at 0.0 V vs SCE as a function of C18SH mole fraction. The average standard deviation bar is 1.0 μC/cm².

spectroscopy. The arguments presented so far would suggest that all C18SH molecules could bind to gold.

To examine this issue further, we have carried out three additional sets of experiments. Figure 6 shows the dependence of current and charge recorded during the LB transfers of C18SH/Cl18H monolayers as a function of the substrate withdrawal rate. Linearity of this plot for rates below 50 mm/min (where one begins to transfer molecules on a thin film of water rather than directly onto gold surface), shows that the time scale of the experiment does not affect the efficiency of C18SH bonding to gold. In the second set of experiments, we measured the total charge collected during LB transfer at 0.0 V vs SCE as a function of C18SH mole fraction in mixed C18SH/Cl18H monolayers. The linearity of the observed charge, shown in Figure 7, proves that all or a constant fraction of C18SH molecules transferred bind to gold.

In the third set of experiments, we have examined the effect of roughness of the gold substrates on the LB transfer ratio and on the charge due to C18SH binding to gold. The latter issue directly addresses the question whether all C18SH molecules transferred onto gold in the LB experiments bind to its surface. Self-assembly of octadecanethiol on gold(111) surfaces is known to result in surface monolayers exhibiting a ca. 30° tilt and a specific registry with respect to the surface gold atoms. A different monolayer structure may be obtained in the case of the LB deposition experiments since the C18SH molecules are transferred in a compressed state where their projected area per molecule on the water surface is only 20.1 Å²/molecule.

The following potentiostatic LB transfer experiments were carried out at 1.5 cm² thin gold foil substrates. Their original surface was smooth but not optically flat. To further increase the extent of surface roughness, we followed a procedure involving repetitive voltammetric cycling of the gold substrates between +1.2 V and −0.3 V vs SCE in 0.1 M KCl. The results are collected in Table 1.

The gold oxide charge (Q0°) in the second column illustrates an increase of true surface roughness of the gold substrates. The third column lists surface roughness relative to Au/glass. As expected, the LB transfer ratios and the charge due to C18SH chemisorption (Q0°) increase with the substrate roughness. This is consistent with the reactive nature of the LB transfer of the C18SH/Cl18H monolayers. However, comparison of the transfer ratios and the QLB values for the two most roughened substrates (entries 4 and 5) indicates that monolayer transfer on excessively rough surfaces no longer follows the microscopic contour of the surface.

Table 1. Dependence of the C18SH Partial Charge Number and the C18SH/Cl18H LB Transfer Ratio on the Roughness of Gold Substrates

<table>
<thead>
<tr>
<th>Substrate Type</th>
<th>C18SH Partial Charge Number (Q0°)</th>
<th>C18SH LB Transfer Ratio (QLB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au/glass</td>
<td>1.00</td>
<td>352</td>
</tr>
<tr>
<td>Au foil</td>
<td>1.09</td>
<td>385</td>
</tr>
<tr>
<td>Au foil</td>
<td>1.22</td>
<td>428</td>
</tr>
<tr>
<td>Au foil roughened</td>
<td>1.35 ± 0.08</td>
<td>619</td>
</tr>
<tr>
<td>Au foil roughened</td>
<td>1.35 ± 0.08</td>
<td>1150</td>
</tr>
</tbody>
</table>

*Charge due to the electroreduction of the surface gold oxide film produced in an anodic voltammetric scan extended to +1.3 V vs SCE in 0.05 M HClO4. Charge due to C18SH chemisorption obtained during potentiostatic LB experiments at +0.30 V vs SCE.

The apparent partial charge number (δ) with surface roughness is the key feature of the data in Table 1. It is clear that δ is higher on rough surfaces compared to relatively smooth Au/glass substrates for which roughness factor is known to be ca. 1.2.50 In view of the finite precision of these measurements, we believe that there are no significant differences between the δ values for the entries 3, 4, and 5 in Table 1. Therefore, we will use their average of 0.36 ± 0.03. Since this average

References:
no longer depends on the increasing roughness of the gold surface, it can be considered to be the true partial charge number of C_{18}SH chemisorption at 0.30 V. This value of \( \delta \) is 24% higher than the apparent partial charge number obtained on the vapor deposited Au/glass substrates. Since the \( \delta \) values were calculated under the assumption of 100% reactivity of the transferred C_{18}SH molecules, the lower value of \( \delta \) on Au/glass substrates indicates that only ca. 81% of C_{18}SH molecules actually chemisorb on gold upon LB transfer. The true partial charge number can, therefore, be obtained by multiplying the values in Figure 5 by 1.24. Thus, they increase from 0.3 at -0.3 V to 0.45 at 0.7 V vs SCE.

This important conclusion requires some discussion. Since it is apparent that the higher surface roughness leads to an increase of the fraction of the thiol molecules capable of chemisorption, we postulate that the LB transfer of a monolayer at high pressures is followed by pressure relaxation and partial respooling of the monolayer before chemisorption of C_{18}SH. These events may, indeed, be necessary to allow the molecules to adopt appropriate surface orientation and/or registry with respect to the surface gold atoms. Such conditions for chemisorption would be met more readily on substrates with certain minimum microscopic surface roughness. Conversely, these conditions may be lacking on surfaces composed, partially, of atomically flat terraces over which monolayer relaxation and respooling may be difficult. It appears that the vapor-deposited Au/glass substrates represent the latter type of surface. The dominance of the 111 domains on vapor-deposited Au films on glass and mica surfaces is well-known in the literature, see also the discussion of the experimentally determined PZC value above).

The preceding discussion leads to a prediction that a higher extent of C_{18}SH chemisorption might also be observed when C_{18}SH/C_{18}OH LB films are transferred at a lower surface pressure. Under such conditions, surface monolayers are in a slightly more expanded state; for example, C_{18}SH mean molecular area increases from 20.1 \( \AA^2/\text{molecule} \) at 20 mN/m to 21.3 \( \AA^2/\text{molecule} \) at 8 mN/m. We have repeated the potentiostatic LB transfer experiments on Au/glass substrates at 0.3 V at 8 mN/m and found, indeed, that a higher charge was transferred compared to 20 mN/m (19.2 \( \pm 1.2 \) \( \mu \text{C/cm}^2 \) was obtained as an average of six runs compared to 15.7 \( \mu \text{C/cm}^2 \) in Table 1). In view of the fact that the LB transfer ratio remained unchanged, this yields a partial charge number of 0.37 \( \pm 0.02 \), a value essentially identical to that in Table 1 after correction for partial chemisorption. This result gives strong support to our explanation of the partial chemisorption of C_{18}SH molecules in LB films transferred at high pressures. We should point out that the higher-surface-pressure conditions are, nevertheless, more advantageous as far as precision and reproducibility of the results are concerned.

We move now to a discussion of a pH effect on alkanethiol chemisorption. In recent reports, Porter and co-workers described a series of electrochemical experiments aimed at desorption of alkanethiols from gold electrodes. Their experiments conducted in 0.5 M aqueous or ethanolic KOH solutions showed well-developed surface voltammetric peaks at negative potentials (e.g., -1.35 V vs Ag/AgCl for octadecanethiol). The authors assigned the charge associated with these peaks to be due to breaking of the thiolate-gold bond. Its value was 1.0 electron per alkanethiol, a value substantially larger than that reported above. It is almost certain, as shown recently by}

![Figure 8. Plot of the charge-transferred due to C_{18}SH chemisorption on gold, and the C_{18}SH partial charge number (corrected for incomplete chemisorption) as a function of pH of the subphase in the LB transfer experiments. Data were obtained at -0.20 V vs SCE in HClO_{4}, NaClO_{4}, and KOH electrolytes. These data represent the difference between the total charge and the double-layer charge (see data in Figure 5). The bar indicates the average standard deviation of 0.80 \( \mu \text{C/cm}^2 \).

Schneider and Buttry,\(^76\) that Porter's interpretation is burdened with a positive error since a significant portion of the voltammetric "desorption" in Porter's experiments is undoubtedly due to a double-layer charge that has to flow to the interface, since desorption of a surface monolayer results in a large increase of its capacitance. Nevertheless, we attempted to carry out our measurements in more alkaline electrolytes (see data in Figure 8). Unfortunately, our experiments could not be done at pH's above 13 due to partial solubility of dissociated octadecanethiol from C_{18}SH/C_{18}OH monolayers on very alkaline subphases. However, considering the rate of the increase of the partial charge number in Figure 8 (corrected for incomplete chemisorption of C_{18}SH as described above), we do not think that its magnitude at pH 14 would be much above its largest value obtained at pH 13. It is interesting to point out that the observed small increase of the partial charge number at and above pH 12 coincides with an expected value of C_{18}SH pK_a at 12.4 and could therefore be explained by an induction effect that allows for a larger fraction of an electron to be donated to gold. This is not inconsistent with our earlier postulate of the coupling via charge-neutrality requirement between the partial electron transfer and the extent of proton dissociation.

Overall, the mechanism of C_{18}SH chemisorption on gold presented in this report is consistent (at least qualitatively) with Porter's electrosorption experiments. Our results could also be compared with the detailed studies of chemisorption of sulfide ions by Schultzze and co-workers\(^79\) and hydrosulfide ions carried out by Briceno and Chandler.\(^80\) Schultzze et al. reported the electrosorption value of S^{2-} on gold to be -2 in the potential range -0.6 to 0.4 V vs SCE. The same value was obtained for HS^- on gold by Briceno and Chandler who also postulated a concurrent dissociation of the hydrosulfide's proton. The transfer of two electrons from sulfide to gold (observed in 1 M NaOH solution) compared with the 0.3 to 0.45 electron transfer accompanying C_{18}SH chemisorption reflects reasonably

well the chemical differences between these two sulfur species. Proton dissociation (and not H₂ release) observed in the chemisorption of HS⁻ is fully consistent with our postulates of partial proton dissociation.

**Partial Charge Number and Electrosorption Valency.** Chemisorption and physisorption at the electrode/solution interface has been an area of considerable importance and a subject of extensive investigations in electrochemistry. The parameter describing the charge supplied to the electrode surface from the external circuit upon adsorption of a species is electrosorption valency or, according to a recent IUPAC recommendation, formal partial charge number, \( \gamma_n \), a quantity defined as

\[
\gamma_n = -1/(F \alpha N / \beta \Gamma) \tag{6}
\]

where \( \alpha \) is the excess charge density at the electrode surface and \( \Gamma \) is the surface concentration of the adsorbed species. In general, adsorption of a species at the electrode surface may result in a change of the excess charge density for two reasons: one stems from an inevitable change (usually a decrease) of differential capacitance of the electrode/solution interface, and the other related to charge transfer between the adsorbing molecule and the electrode. The IUPAC recommended term for the latter, which may be negligible (as in physisorption), is partial charge number. It is important to note that the formal partial charge number is the only quantity accessible experimentally. This is because chemisorption of molecules at the electrode/solution interface simultaneously causes both effects mentioned above. In other words, the partial charge number can be measured only when adsorption does not affect the structure of the double-layer—a virtually impossible scenario. We believe that the LB transfer experiment carried out under potentiostatic conditions described in this report creates experimental conditions that allow, for the first time, a direct determination of the partial charge number independently of the double-layer capacitance component. This is accomplished by allowing chemisorption to occur only at the triple-phase contact line as the electrode surface is emersed dry from the electrode solution (see Figure 1). Thus the structure and the capacitance of the electrode/solution interface are never perturbed. The double-layer charge of the electrode/solution interface, as demonstrated above, can also be measured independently in a parallel experiment involving physisorbed species (C₁₈OH). The measurements of the double-layer charge density by the LB transfer of C₁₈OH monolayer, followed by the total charge measurements with mixed C₁₈SH/C₁₈OH monolayers, and a calculation of the partial charge number for C₁₈SH adsorption on gold as a difference of the two constitute an illustration of this approach. The only limitation of this approach, besides its precision which is admittedly not as high as impedance or chronocoulometric methods, is the requirement that the adsorbent be insoluble in water. This would require one to work, for example, with long alkyl chain derivatives of adsorbents of interest.

**Conclusions**

We have developed a coulometric technique that combines Langmuir–Blodgett monolayer transfer with constant potential current measurements. This technique can be used to measure charge associated with a transfer of a monolayer from the air/water interface onto a conducting substrate under potentiostatic conditions. In cases of weak monolayer/substrate interactions (physisorption), this charge corresponds to the double-layer charge density on the substrate/solution interface, before the LB transfer. In cases of chemisorption, a sum of the double-layer charge and the charge transferred between the molecules in the monolayer and the substrate is obtained. The latter is illustrated in this report by LB transfer of C₁₈SH/C₁₈OH. In this case, the difference between the total charge and the double-layer charge, which can be obtained independently in the experiments involving weakly interacting C₁₈OH, gives the partial charge number of the chemisorbed species, C₁₈SH. Thus this technique allows one, for the first time, to obtain partial charge number under conditions where chemisorption and the measurements of the related charge transfer are not perturbed by the otherwise inevitable changes of the double-layer capacitance that normally accompany adsorption at the electrode/solution interface.

We have investigated the potential dependence of C₁₈SH chemisorption on vapor-deposited gold films on glass. The C₁₈SH partial charge number increases from 0.30 at -0.30 V to 0.45 at 0.70 V vs SCE. Thus C₁₈SH binding to gold involves formation of a coordination type bond whose character depends weakly on the potential of the gold substrate. Clearly, this mechanism does not involve gold oxidation, as postulated in the literature, nor does it postulate reduction of proton or oxygen (eqs 1-3). It is well-known that in the potential range investigated in this study the gold surface is in a reduced state. To maintain electroneutrality of the surface monolayer upon its transfer on gold and above the water surface, we postulated that the charge transferred due to chemisorption is coupled to partial proton dissociation of the thiols. The release of protons is also consistent with weakening of the S–H bond caused by thiol bonding to gold but its extent is governed quantitatively by the magnitude of the partial charge number via the electroneutrality requirement.

Investigations of the effect of the surfaces roughness of the gold substrates on the LB transfer ratios and the apparent partial charge number revealed that only approximately 81% of the C₁₈SH chemisorb to gold when a compressed C₁₈SH/C₁₈OH LB monolayer is transferred onto vapor-deposited Au/glass substrates. We postulate that inability of the C₁₈SH molecules that were transferred in an ordered array onto a flat gold substrate to assume appropriate orientation and/or registry with the surface gold atoms may be responsible for this incomplete chemisorption. Electrochemical roughening of the surface apparently alleviates this problem by allowing the molecules to respread and readjust their registry and tilt with respect to the substrate surface due to its microscopic roughness. Consistent with this postulate, we determined that LB transfer done at a lower surface pressure also results in an increase of the partial charge number and in the full extent of chemisorption. The values of the partial charge number given above include the correction for the incomplete chemisorption on Au/glass substrates.

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